Dilute Sulfuric Acid Pretreatment of Corn Stover in a Pilot-Scale Reactor: Investigation of Yields, Kinetics, and Solids

Enzymatic Digestibilities

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Introduction

- Dilute sulfuric acid pretreatment of corn stover was performed in a continuous pilot-scale reactor
- Data was collected on xylose hydrolysis yields and enzymatic digestibilities of the pretreated cellulosic solids
- The xylose yield data was used to calculate kinetic rate parameters for a biphasic xylan hydrolysis model incorporating formation of intermediate xylo-oligomers

Materials and Methods

- Corn stover
  - Used approximately 9 month old stover that was tub-ground and washed and dried to 10% moisture
- Analytical
  - Performed solids compositional analysis of raw and pretreated solids
  - Liquor
    - Measured concentration of monomeric and total sugars, acetic acid, furfural, and HMF by HPLC; measured pH
  - Measured insoluble solids in the pretreated slurry
- Enzymatic digestibility
  - SSF was performed on the washed pretreated solids at 6% cellulose loading, 15 FPU/g cellulose enzyme loading, 32°C
  - Calculated cellulose conversion from ethanol yield results

Pretreatment

- 41 pretreatments runs at a variety of conditions were conducted in a continuous 1 dry ton/d pilot-scale reactor (see flow diagram)
- Pretreatment conditions
  - 165-183°C
  - 3-12 min
  - 0.5-1.4% (w/w) nominal acid concentration
  - 20% (w/w) total reactor solids concentration

Pretreatment Experimental Protocol

- Steady state operating conditions were established and then samples were taken; data acquisition system collected sensor data every 30s
- Samples taken
  - Raw feedstock (for moisture)
  - Pretreated slurry
  - Vapor vent streams
- Calculations
  - Xylan hydrolysis yields (monomeric and oligomeric xylose, furfural, unconverted xylan) were calculated from stream composition and flow rate data
  - Results were also analyzed using a combined severity factor (CSF)

$$CSF = Log_{10}\left[t \times \exp\left(\frac{T - 100}{14.75}\right)\right] - pH$$

Dilute Acid Kinetics

$$\begin{array}{l} \textit{Fast reacting xylan} \xrightarrow{k_1} \\ \qquad\qquad\qquad\qquad \textit{Xylose oligomers} \xrightarrow{k_3} \textit{Xylose} \xrightarrow{k_4} \textit{Decomposition product} \\ \textit{Slow reacting xylan} \xrightarrow{k_2} \end{array}$$

$$k_i = \{k_i^o + k_i^H (10^{-pH})\} \exp\left(\frac{-E_i}{RT}\right)$$

An Excel add-in (Evolver) using a genetic algorithm was used to estimate the parameter values (fast hydrolyzing xylan fraction, k_i^o, k_i^H, and E_i) by minimizing an error term composed of the sum of the square of the errors between measured and predicted values for monomeric and oligomer xylose and unconverted xylan.

Pretreatment System

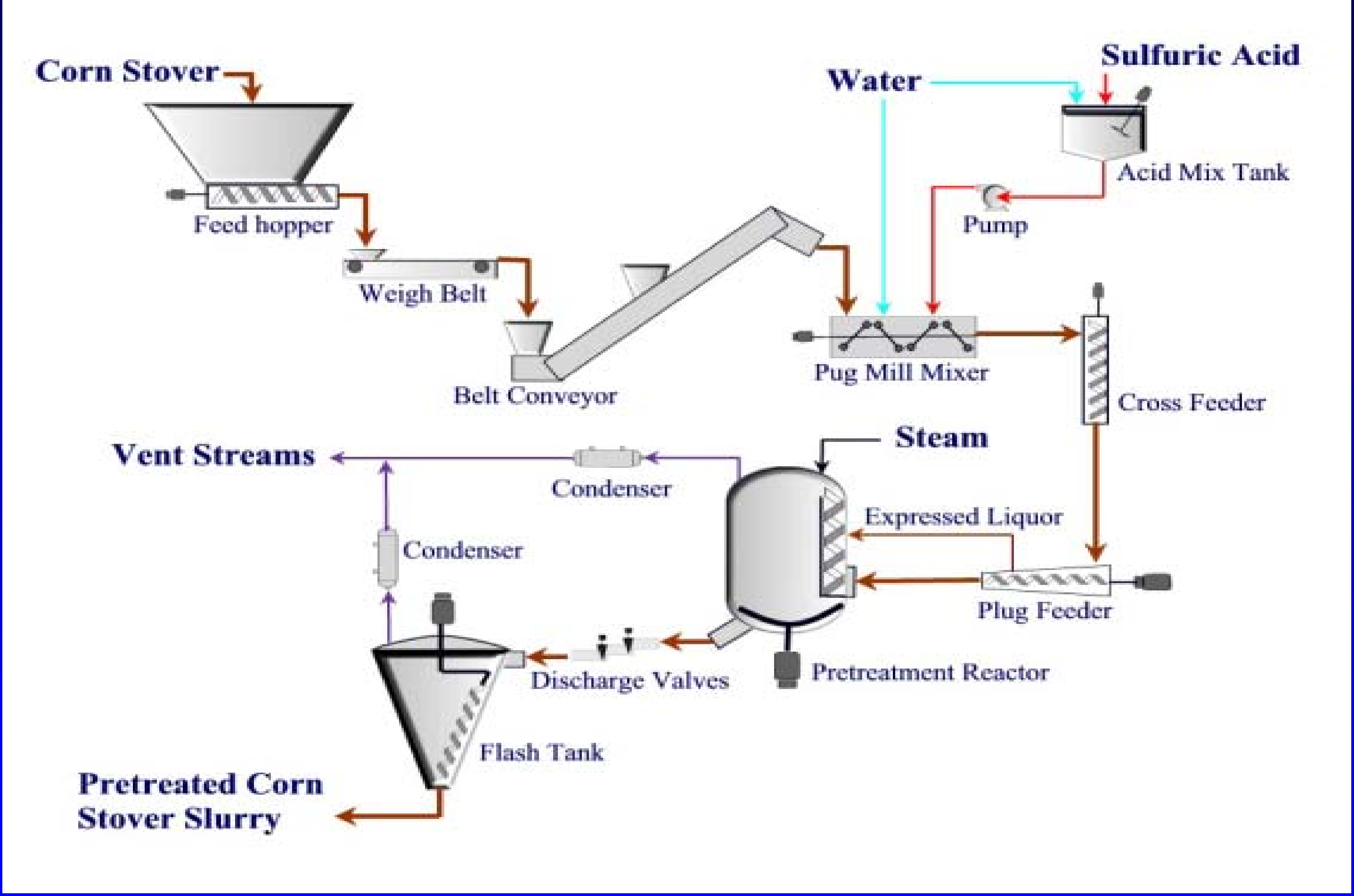


Figure 1. Monomeric and Total Xylose Yields

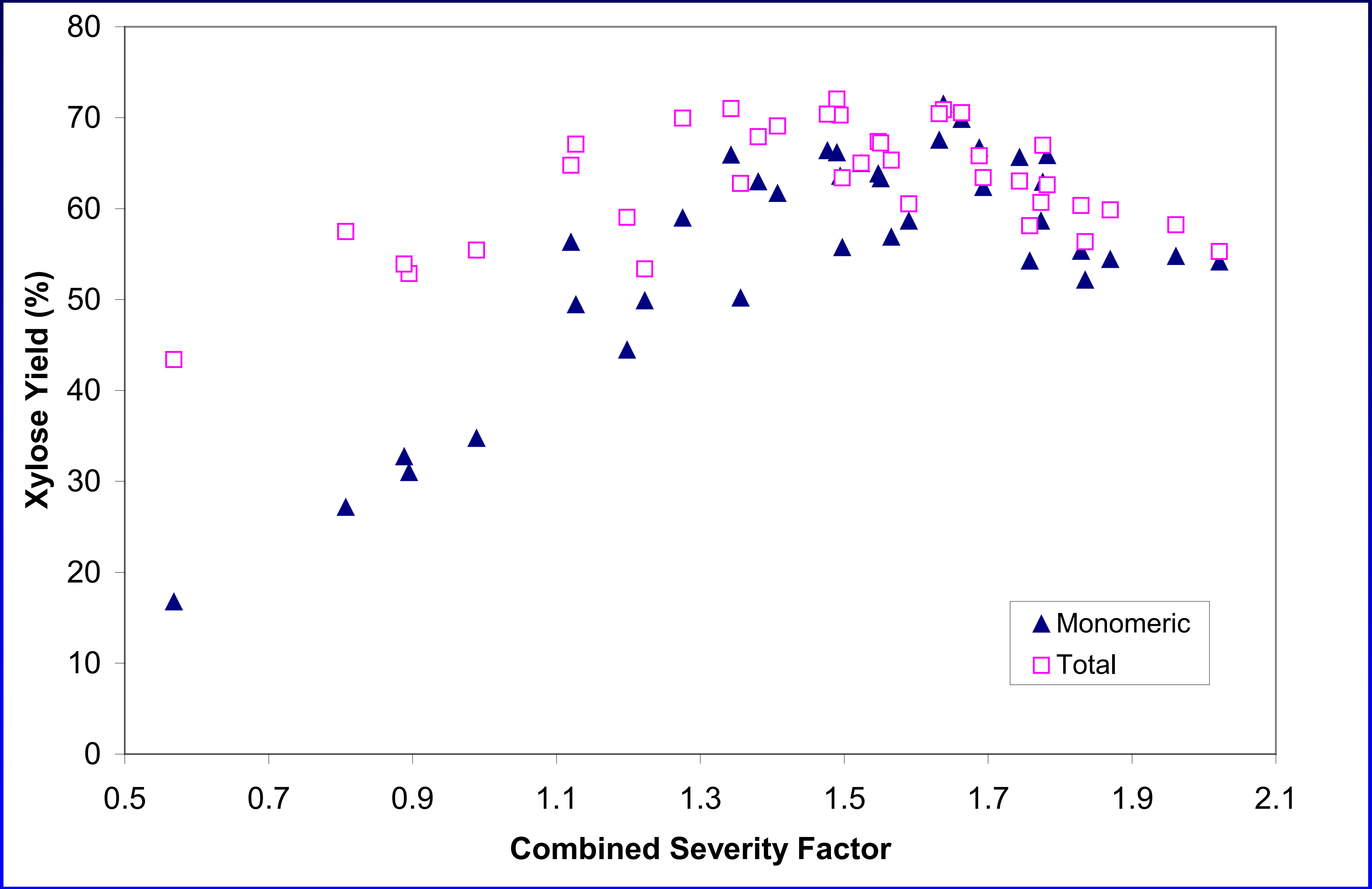


Figure 2. Xylan Fractionation and Mass Balance Closure

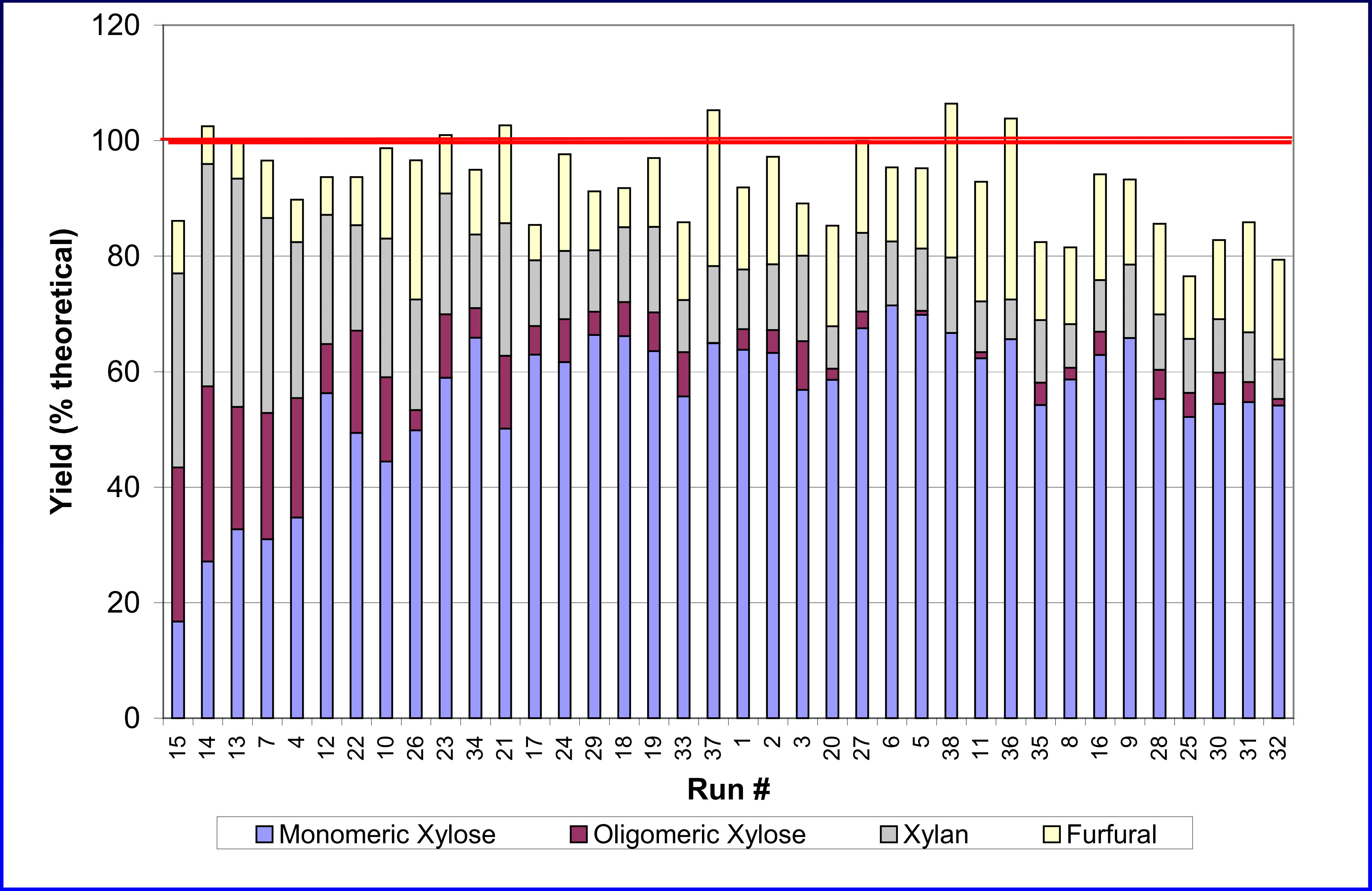
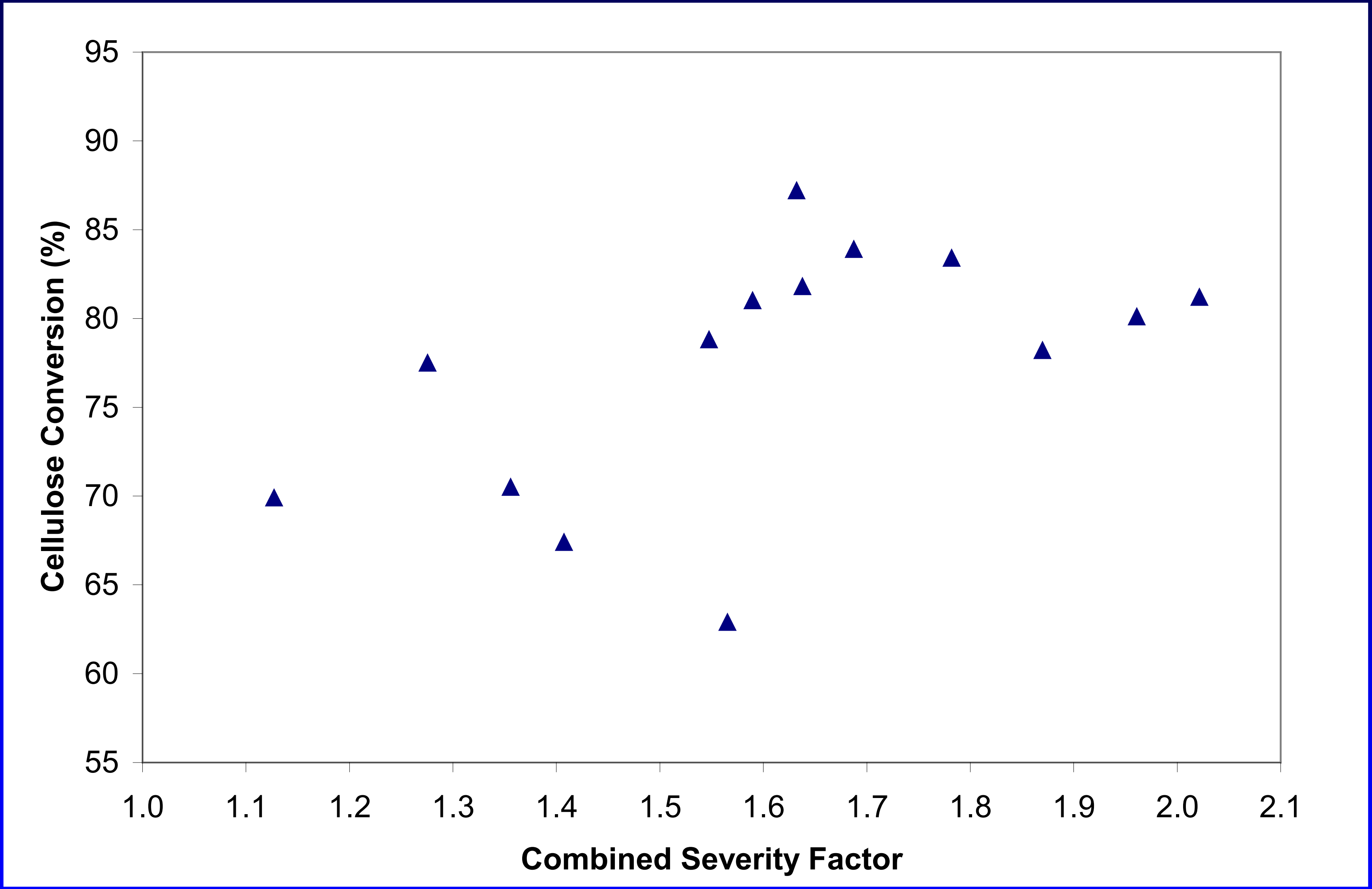


Figure 3. Enzymatic Digestibilities



Highlight Results - Experimental

- Monomeric and total xylose yields reach a peak of 70-71%, but at different pretreatment severities (Fig. 1)
- With increasing severity, furfural yields increase and unconverted xylan and oligomeric xylose yields decrease (Fig. 2)
- Mass balance closure ranges from 85-105%, but are significantly lower at higher severities (Fig. 2)
- Cellulose conversion increases with increasing severity reaching a value of 87% (Fig. 3)

Figure 4. Predicted versus Experimental Yields

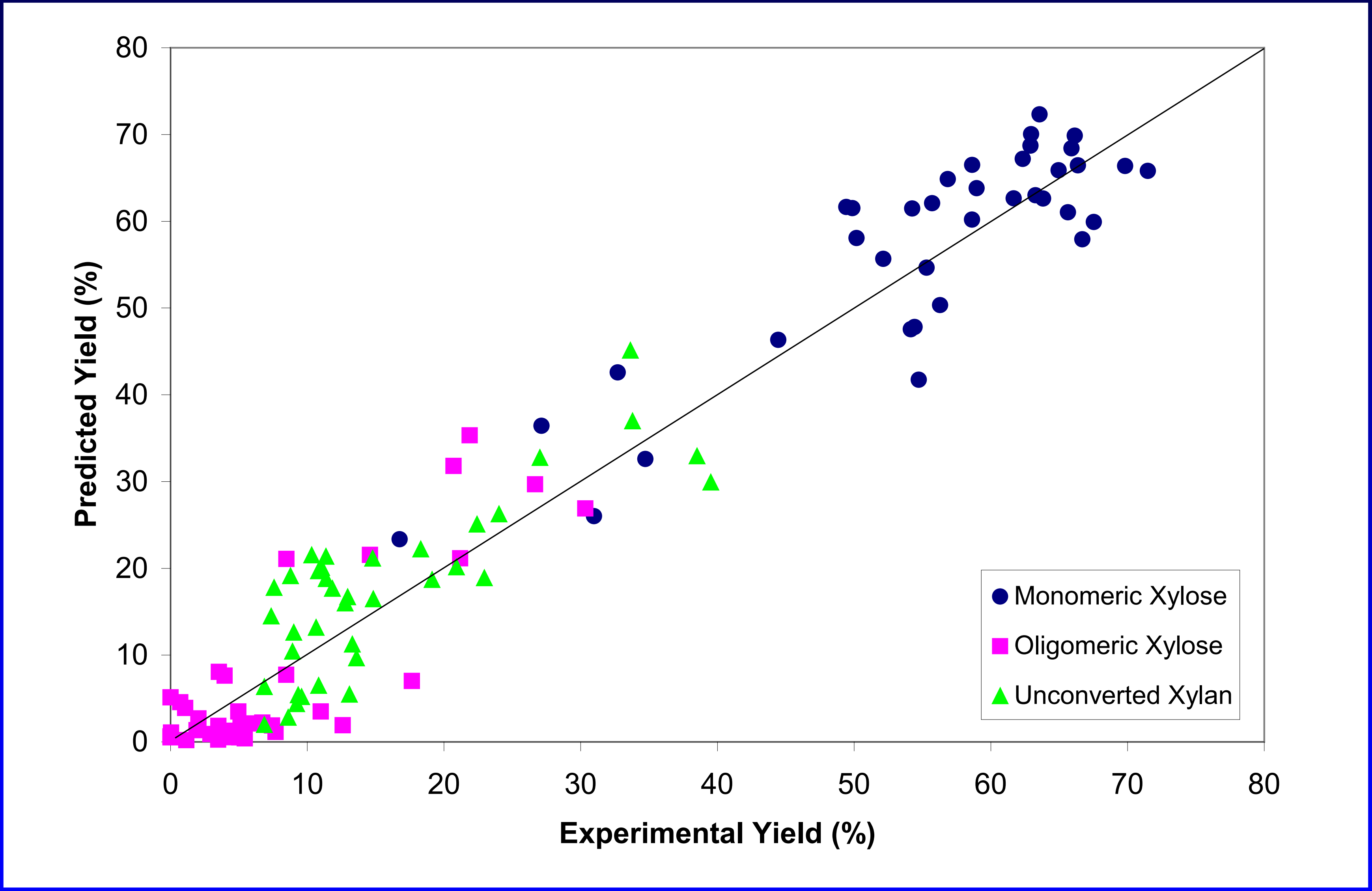


Figure 5. Kinetic Modeling Results: Based on Maximizing Monomeric Xylose

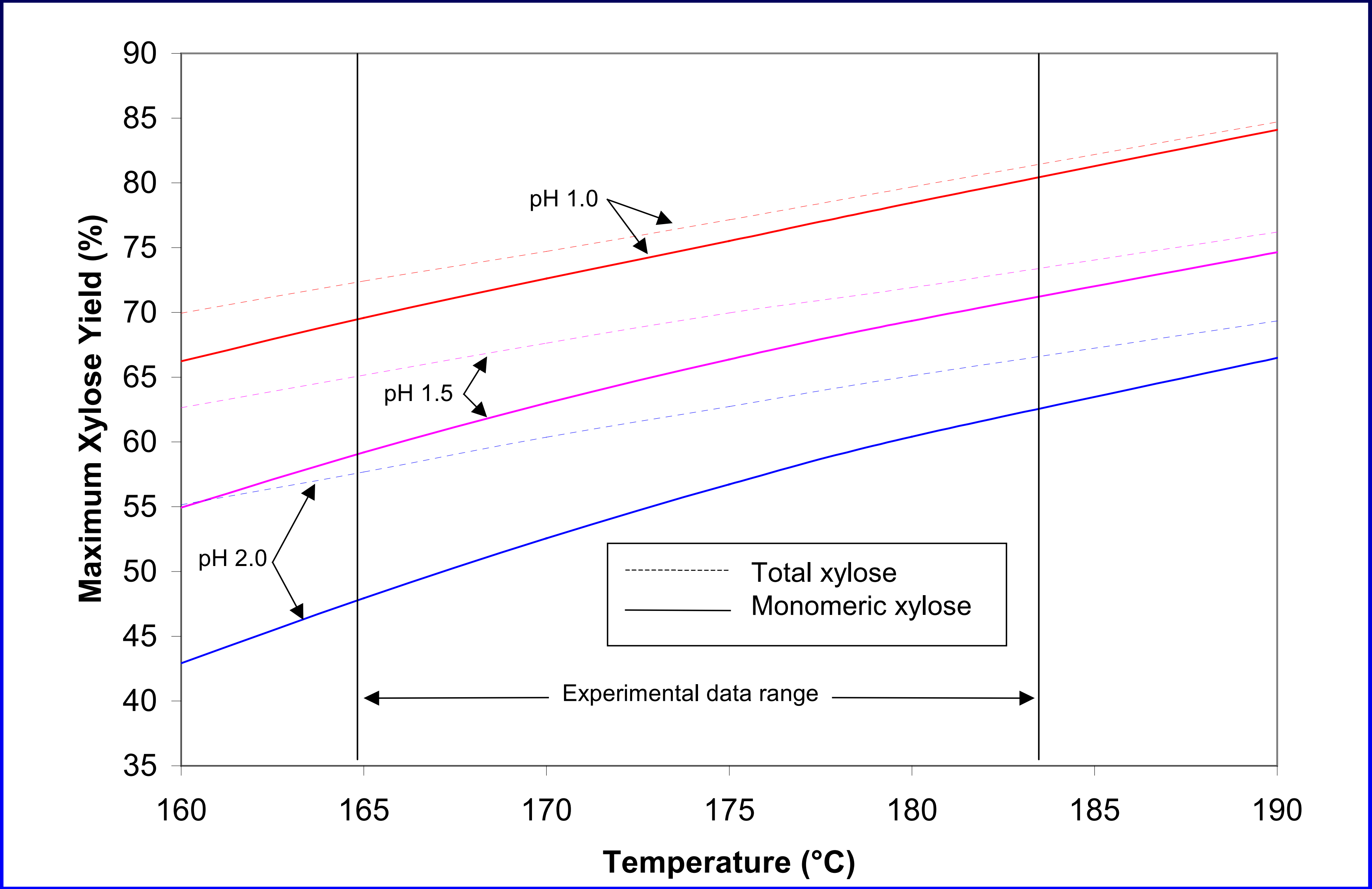
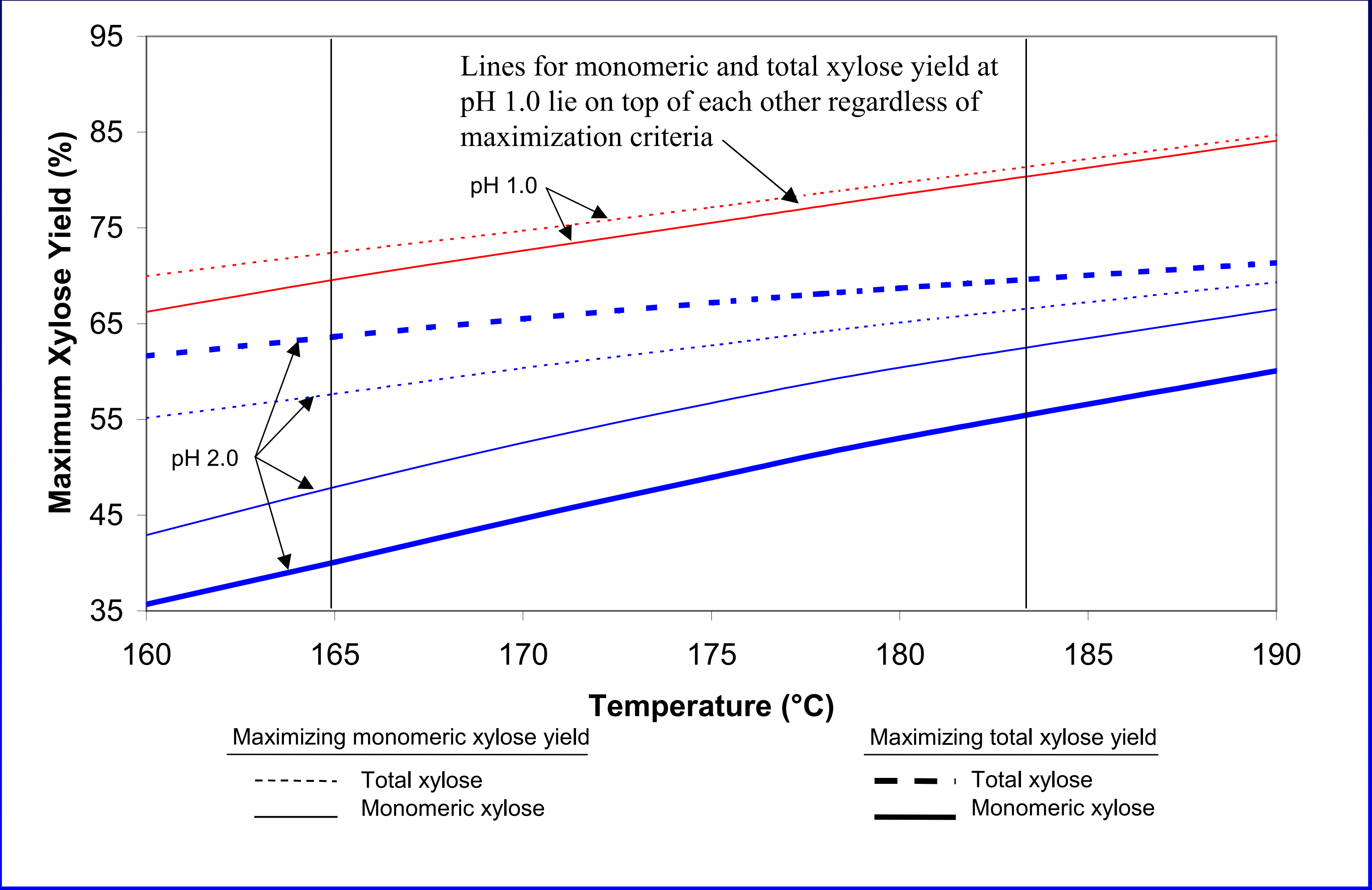


Figure 6. Kinetic Modeling Results Based on Maximizing Monomeric or Total Xylose



Highlight Results - Kinetic Model

- The kinetic model predicts xylan hydrolysis performance across the data set fairly well (Fig. 4)
- Low pH and high temperatures are required to achieve the highest xylose yields (Fig. 5)
- Total xylose yields are greater than monomeric xylose yields, although the differences are small at low pH (Fig. 5)
- At low pH, xylose yields are the same regardless of which criteria is used to maximize yields (Fig. 6)
- At high pH, higher total xylose yields can be achieved by maximizing on total xylose (Fig. 6)

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